Presented at the 80th Annual APCA Meeting,
New York, NY, June 21-26, 2987.

Submitted to JAPCA August 1987.

# Speciation of Arsenic in Ambient Aerosols Collected in Los Angeles

Erlinda S. Rabano, Norma T. Castillo, Kahirup J. Torre

Atmospheric Testing Branch
Haagen-Smit Laboratory Division
State of California
Air Resources Board
9528 Telstar Avenue
El Monte, CA 91731

Paul A. Solomon
Environmental Quality Laboratory
California Institute of Technology
Pasadena, CA 91125

Abstract

First time measurements, in the Los Angeles area, of the potentially toxic inorganic species of arsenic (arsenite and arsenate) have been obtained in fine (< 2.5 μm AD) and coarse (> 2.5 μm AD) atmospheric particles. A recently developed method -- which included procedures for sample collection, preparation, and analysis -- was used in this study. In this method, size-fractionated aerosol samples were collected using a high-volume dichotomous virtual impactor which employed PTFE filters. A section of each filter was leached in $10^{-4}$ N HCl for 1 hour at 85°C. The concentrations of As(III) and As(V) were then determined from a single sample aliquot by a two-step reduction procedure employing Zn metal powder and $NaBH_4$. The arsenic species produced during each reduction step (arsine) was then detected by flame atomic absorption spectroscopy. Using this method, results were obtained for the recovery of arsenic standards added to unexposed and collected filters. These data indicated this method can be used to quantitatively determine concentrations of As(III) and As(V) in atmospheric particulate matter samples. Size-fractionated aerosol samples were collected in the City of Industry during January and February of 1987. In most samples, As(III) and As(V) were above the detection limit (approximately 1 ng $m^{-3}$ of either species) in both aerosol size-fractions. A greater portion (about 75 percent) of the two species were observed in the fine particles. The As(III)/As(V) ratio for both particle sizes was close to 1 (i.e., an equal mixture of both species). Comparison of total TSP arsenic determined by the speciation method, to that measured by a routine California Air Resources Board approved procedure showed good agreement ($r = 0.95$), indicating both methods were approximately equivalent for the collection and analysis of aerosol arsenic.

## Introduction

California's air toxic law became effective in January, 1985, and defines California's air toxic program (Health and Safety Code Sections 39650 et seq.).[1] Under this legislation, a statutory mandate was created for the identification and control of toxic air contaminants found in California.

One of the mandated criteria used in the identification process to prioritize compounds which are believed to be hazardous to human health is its ambient concentration. The California Air Resources Board (CARB) has developed a list of potentially toxic substances to enter the identification phase of this program based on the mandated ambient criteria. One such element under consideration is arsenic. The measurement of individual species of this element is particularly important because of the variations in toxicity and carcinogenity of the different arsenic compounds found in the environment [i.e., As(III) is not only more toxic, but it also represents a greater carcinogenic hazard than As(V)].[2-5]

Arsenic is emitted into the atmosphere from both anthropogenic and natural sources and is present in only trace amounts. Its atmospheric concentration ranges from about 0.01 - 0.1 ng $m^{-3}$ in clean areas such as Antarctica[6] and up to 500 ng $m^{-3}$ near certain industrial environments such as copper smelters.[7] The average measured arsenic level in U.S. urban areas is approximately 20 ng $m^{-3}$.[8] Of the sources known and estimated for arsenic emissions in the Los Angeles area it appears the primary source of arsenic, approximately 33 kg per day, is from stationary high temperature combustion processes (e.g., glass furnaces, primary metallurgical processes, and fuel oil combustion).[9] This is important since several workers[10,11] suggest $As_4O_6$ (note, $As_2O_3$ sublimes to form the gas phase species $As_4O_6$) is the predominant arsenic species emitted into the atmosphere from these types of industrial sources.

A variety of analytical methods currently exist for measuring total arsenic at concentrations present in the atmosphere. However, to date, only a method proposed by Solomon concentrated on determining the inorganic species of arsenic [arsenite, As(III); arsenate, As(V)] in atmospheric particulate matter.[12] In that study, particular attention was given to the measurement of these species while maintaining the initial As(III)/As(V) ratio during the sample collection, preparation, and analysis steps. An analytical detection limit of 25 ng was obtained for either species in a given sample aliquot. An average As(III)/As(V) ratio was reported for total suspended particulate matter (TSP) collected in Tucson, Arizona of about 0.31 $\pm$ 0.29 with a range from less than 0.04 to 0.97. The average atmospheric concentrations of As(III) and As(V) were about 1.6 $\pm$ 1.4 ng $m^{-3}$ and 5.4 $\pm$ 3.3 ng $m^{-3}$, respectively.

To help assess the impact of these potentially toxic species on human health, size-fractionated samples of atmospheric particulate matter should be obtained, with an emphasis on particles which are most efficiently collected in the lungs (i.e., particles less than 2.5 m aerodynamic diameter).[13,14] A preliminary study, employing the commercially available low-volume virtual dichotomous sampler (VDS) (model 241, Sierra-Andersen Corp., Inc.), indicated this sampler collected an insufficient amount of material for the analysis of As(III) and/or As(V) by the sensitive analytical method reported by Solomon. In addition, replicate analysis could not be performed, since the entire filter sample was used to obtain maximum sensitivity. To help overcome these problems, a high-volume dichotomous virtual impactor (HVDVI) was employed.[15] This sampler collects up to 30 times the mass of efficiently size-fractionated material and has a sample-to-blank ratio which is 2 times greater than the VDS.

The objective of this work was to verify the method reported by Solomon[12] for the collection and analysis of inorganic species of arsenic (arsenite and

arsenate) in size-fractionated samples of atmospheric particulate matter collected in the Los Angeles area. Samples were collected employing the HVDVI and a collocated standard high-volume sampler. The latter is used for routine monitoring of total suspended particulate matter by the State of California Air Resources Board. Experiments were carried out to examine the efficiency of recoveries of aqueous arsenite and arsenate standards added to both unexposed filters and to filters containing aerosol particles.

Experimental

## Atmospheric Particulate Matter Collection

Atmospheric particulate matter samplers were sited on the roof of the two-story U.S. Post Office building located in the middle of an industrial area in the City of Industry, Los Angeles County, California. Previous routine monitoring by the CARB indicated high ambient concentrations of total arsenic can typically be found in this area.

Two samplers were employed at this site. One was a standard high-volume aerosol sampler (hi-vol)[16] that employed 8 x 10 in. Whatman glass microfiber filters and operated at a flow rate of about 1.1 $m^3$ $min^{-1}$. This sampler collected total suspended particulate matter and is currently employed by the CARB for routine aerosol monitoring of many atmospheric species. The other sampler was a high-volume dichotomous virtual impactor[15] which collected atmospheric particles in two size ranges (fine and coarse) on 102 mm polytetrafluoroethylene (PTFE) filters (Zefluor, 2.0 μm Gelman Sciences). It should be noted this particular filter type (Zefluor from Gelman Sciences) required several rinsings in deionized, metal-free water prior to sample collection to obtain reliable, reproducible results.

The HVDVI, when operated at about 400 l $min^{-1}$, has a cutpoint (50 percent collection efficiency) of about 2.5 μm aerodynamic diameter (AD). Thus, the fine particle filter collected particles less than 2.5 μm AD, while the coarse particle filter collected particles greater than 2.5 μm AD.

Immediately following sample collection, the loaded filters were removed from the sampler and brought back to the lab. The HVDVI filters were placed individually into glass petri dishes, sealed, and then placed into plastic zip-lock baggies. The samples were then stored in a freezer from one day to several weeks until they were analyzed.

## Sample Preparation and Analysis

Two sample preparation procedures for determining the inorganic species of arsenic were tested. Method A was the original semimicro technique developed by Solomon.[12] Method B was a modification of the original method wahich allowed for the leaching of a larger portion of the collected filter sample. A third preparation method was employed for the analysis of total arsenic collected on glass fiber filters.

Arsenic Speciation. In method A, one-eighth of the 102 mm Zefluor filter was sectioned and placed in a 7 ml Teflon vial fitted with a threaded screw cap (Savillex Corporation). For PTFE filters, 0.05 ml of 100 percent ethanol was pipetted directly onto the filter surface. This was done to reduce the hydrophobic nature of the PTFE material and to allow for the interaction of the leaching solution with the sample.[17] A PTFE rod (3/8 x 1/2 in.) was then placed on top of the filter pieces to keep them submerged and 2.0 ml of $10^{-4}$ N HCl was added. The Teflon container was closed tightly and placed in an oven at 85°C to 90°C for 1 hour. The vial and sample were allowed to cool to room temperature before analysis. A 1.0 ml aliquot of the sample leachate was then analyzed for As(III) and As(V) by the Zn-$NaBH_4$ method described below.

In method B, up to one quarter of the filter was sectioned and placed in a 15 ml Teflon vial fitted with a threaded cap. As above, 0.05 ml of 100 percent ethanol was added directly onto the filter surface followed by a slightly larger PTFE rod. Ten ml of $10^{-4}$ N HCl was added to the Teflon container, closed tightly, and then placed in an oven at about 85°C for one hour. The sample was allowed to cool to room temperature, after which the entire leachate was poured into a 50 ml pyrex beaker. Immediately following, 10 ml of 8.5 N HCl was added to the leachate to obtain a final normality of 4.25 N HCl in 20.0 ml. The sample remained in the pyrex beaker up to several hours until the entire volume

(20.0 ml) was added to the reaction flask. The sample was then analyzed for As(III) and As(V) by the Zn-$NaBH_4$ procedure described below.

In the Zn-$NaBH_4$ analysis procedure, As(III) and As(V) were efficiently separated in a two-step reduction process from a single sample aliquot in a solution of HCl. In the first reduction step, a slurry of Zn metal powder was used to reduce As(III) to arsine ($AsH_3$). Immediately following the end of the first reaction, $NaBH_4$ was used to reduce As(V) to $AsH_3$. The arsine produced during each step was detected in an $N_2$-$H_2$ air-entrained flame of an atomic absorption spectrophotometer (Model 3030, Perkin-Elmer Corporation). A complete description of the apparatus and experimental conditions used can be found in the literature.[12] When employed by this laboratory, the above procedure resulted in a routine (day-to-day) analytical detection limit for either species of about 25 ng. The direct analysis of aqueous arsenite and arsenate mixed standards by this method resulted in a precision for the analysis of As(III) and As(V) of 11 and 9 percent, respectively, at 100 ng of each species, and 2 and 4 percent, respectively, at 500 ng of each species.

Total Arsenic. A procedure (Method 107) developed by the CARB's Haagen-Smit Laboratory was used for the analysis of total arsenic.[18] In this procedure, one quarter of a glass fiber filter was sectioned and placed into a 100 ml graduated mixing cylinder to which 50 ml of 0.5 N $HNO_3$ was added. The cylinder and contents were placed in an ultrasonic bath (450 watts) for 1 hour at about 70°C. After that time, 50 ml of deionized, metal-free water was added, and the contents were leached for a second hour. The sample was filtered and a 0.02 ml aliquot was analyzed for total arsenic by graphite furnace atomic absorption spectroscopy (Model 3030, Perkin-Elmer Corporation).

Standards and Reagents. Arsenic(III) standards were diluted daily from a 1000 mg $l^{-1}$ stock solution of As(III) which was prepared from $As_2O_3$ and obtained directly from VWR Scientific (arsenic reference standard solution, VWR Scientific). The As(V) standards were diluted daily from a 1000 mg $l^{-1}$ stock solution of As(V) which was prepared from $As_2O_5$ and obtained directly from EM Reagents (1000 $\pm$ 0.002 gm $l^{-1}$ of As in water, EM Reagents). Sodium tetrahydridoborate pellets ($NaBH_4$, 99 percent purity, 10/32 inch, Alpha Products) each weighing approximately 0.25 gm and Zn metal powder (8 micron, 99.9 percent pure, Aesar) were used as the reductants. Concentrated hydrochloric acid (reagent grade) with no measurable arsenic blank was obtained from Baker (Baker Chemical Company). All solutions were prepared in deionized, metal-free water (Milli-Q, Millipore Corporation).

Results and Discussion

Two sample preparation methods (A and B) for the dissolution of arsenite and arsenate from PTFE filters were tested to obtain the most sensitive, accurate, and reproducible results. Method A was the original semimicro procedure developed by Solomon[12], while a slightly modified procedure, Method B, was used to leach a larger portion of the collected filter.

The effect of the amount of ethanol pipetted directly onto the PTFE filter surface, prior to leaching the sample, was studied for both preparation procedures. For Method A, improved recoveries for each arsenic species (i.e., about equal to the amount of arsenic added to the filter) were observed when ethanol (0.05 ml) was added to unexposed filters, relative to when no ethanol was employed. This was similar to results observed by Solomon.[12] Different observations were found when Method B was used. In this case, the best recoveries (i.e., approximately equal to the amount of arsenic added to the filter) were obtained when no ethanol was added to the unexposed filter. As the amount of alcohol pipetted onto the filter surface was increased from 0.05 to 0.2 ml, the amount of As(III) observed decreased to less than 10 percent, while the amount of As(V) observed increased to about 150 percent. A mass balance of the two arsenic species suggested that when Method B was employed As(III) was being oxidized to As(V).

Table I reports results for a limited number of experiments, comparing the recovery of standards added to unexposed filters for Methods A and B. In each case, an aqueous standard containing equal amounts of As(III) and As(V) (in the range of 200-600 ng) was pipetted directly onto the filter surface. As can be seen, excellent recoveries were obtained for Method A. For Method B, As(III) recoveries were lower than expected, whereas As(V) recoveries were higher. These results suggested that a fraction of As(III) was oxidized to As(V) during

the sample preparation and analysis steps. As discussed previously, the observation of this effect for Method B may have been due to the addition of the ethanol, since 0.05 ml of ethanol was used in these recovery experiments.

Aqueous standards, similar to those added to the unexposed filters, were also directly pipetted onto the particles of collected filters. These filter samples were analyzed by Method A. The average recovery of As(III) and As(V) (including both the fine and coarse aerosol fractions) was 79 $\pm$ 22 percent, respectively. These results suggested that the complex matrix of collected particulate matter may slightly affect the measurement of the individual arsenic species. Similar results (i.e., a slight change, up to about 20 percent) have been previously reported.[12] Therefore, to obtain the most accurate results, the method of standard additions can be used to compensate for these small changes.

Results obtained from the two types of recovery experiments (i.e., recoveries from unexposed and collected filters) can be used to estimate the precision for the combined sample preparation and analysis procedure (Method A). The estimated error for As(III) and As(V) in both size fractions ranged from about 8 percent for unexposed filters to about 23 percent for filters containing particles. The larger error obtained from loaded filters was most likely due to the effect that variations in the complex matrix of the collected particles can have on the analysis of As(III) and As(V).

Concentrations of arsenic [sum of As(III) and As(V)] measured in total suspended aerosol (i.e., total TSA arsenic) collected by the HVDVI (sum of fine and coarse fractions) and the standard high-volume sampler are presented in Table II. Samples collected by the HVDVI were analyzed according to Method A, while those collected by the standard high-volume sampler were analyzed by the total arsenic procedure (CARB method 107).[18]

As can be seen in Table II, the concentration of total arsenic observed in samples collected by the HVDVI ranged from < 1.1 to 74.1 ng $m^{-3}$ with a mean and standard error of the mean of 15.7 $\pm$ 4.4 ng $m^{-3}$. Values reported for samples collected by the hi-vol sampler range from 2.8 to 69.4 ng $m^{-3}$ with a mean and standard error of the mean of 18.9 $\pm$ 4.3 ng $m^{-3}$. The average ratio of total TSA arsenic collected by the HVDVI to that of the hi-vol sampler was 0.86. Linear regression analysis (hi-vol versus HVDVI) of these data yielded a slope and intercept of 1.0 and -3.2, respectively and a correlation coefficient (r) of 0.95 (n=16). This agreement was very good considering the two samplers employed different collection substrates, the samples were prepared and analyzed by different methods, and the samples probably have different inlet collection efficiencies.

With respect to the collection by different filter substrates, it should be noted that, while PTFE filters are virtually inert, gas phase oxyacids of arsenic (most likely $As_4O_6$) may be adsorbed and even oxidized by the more reactive glass fiber filter substrate. This would result in a positive artifact for aerosol arsenic. Similar results of positive artifact formation on glass fiber filters have been reported for the collection of aerosol nitrate and sulfate. In these cases, the oxyacids of nitrogen and sulfur (NO, $NO_2$, $HNO_3$, and $SO_2$) are adsorbed, or adsorbed and oxidized by the reactive filter material.[19-21]

Table III presents the As(III) and As(V) concentrations (ng $m^{-3}$) measured in the fine and coarse particle fractions collected in the City of Industry from 12 January to 3 February 1987. All analyses were performed using sample preparation and analysis Method A. Arsenic(III) was observed on all but two filters in the fine particle fraction, while it was above the detection limit on only about half the collected coarse particle samples. Arsenic(V) was measured

on about 85 percent of the collected coarse and fine particle samples. On the average, approximately 25 percent of the As(III) and 42 percent of the As(V) were observed in the coarse particle fraction. This is a larger fraction then one would typically expect if the major source of arsenic, in the Los Angeles area, was from high temperature combustion processes[9] (i.e., these sources predominantly emit As(III) as gas phase $As_4O_6$[9,10]) and if only gas-to-particle conversion processes were occurring. However, arsenic(III) oxide may be behaving similar to the gas phase precursors of particle nitrate and sulfate [i.e., the oxyacids of nitrogen (e.g., NO, $NO_2$) and sulfur (e.g., $SO_2$) respectively] both of which exhibit coarse particle modes in the South Coast Air Basin.

The ratio of As(III)/As(V) is also presented in Table III for each sample. The average of this ratio was greater than one for the fine particles and slightly less than one for the coarse particles. For samples where both species were above their minimum detectable level, the As(III)/As(V) ratio ranged from about 0.5 to about 2.9 in both the fine and the coarse particle fractions. These results are somewhat different from those obtained in Tucson, Arizona.[12] In that study, the average As(III)/As(V) ratio observed in total suspended particulate matter, collected by a hi-vol sampler employing quartz fiber filters, was about 0.3 with a range from less than 0.04 to 0.97. These differences were most likely due to the impact of the various sources in the surrounding areas, on the age of the aerosol measured at the sampling sites, and/or on the rate at which As(III) was oxidized in the atmosphere (i.e., variations in the effective oxidation potential of the atmospheric environment).

Summary and Conclusion

A recently developed method[12] for the determination of inorganic species of arsenic (arsenite and arsenate) in atmospheric particulate matter was applied to aerosols collected in the Los Angeles area. Fine (< 2.5 μm AD) and coarse (< 2.5 μm AD) particle samples were collected in the City of Industry by a high-volume dichotomous virtual impactor (HVDVI). The use of this sampler allowed for the collection of a sufficient amount of sample so both As(III) and As(V) could be routinely detected in both size-fractions. In addition, use of the HVDVI, instead of the comercially available low-volume virtual dichotomous impactor, allowed for replicate analyses on individual filter samples. This is important, since more accurate results for the analysis of As(III) and As(V) can be obtained by applying the method of standard additions.

After sample collection, a section of each filter was leached in $10^{-4}$ N HCl for one hour at 85°C. The concentrations of As(III) and As(V) were then determined from a single sample aliquot by a two-step reduction procedure employing Zn metal powder and $NaBH_4$. The arsenic produced during each reduction step (arsine) was then detected by flame atomic absorption spectroscopy.

Results obtained from recovery experiments, where arsenic standards were directly added to unexposed and collected filters, indicated this method can be used to quantitatively determine concentrations of As(III) and As(V) in atmospheric particulate matter samples collected in the Los Angeles area. In addition, comparison of total TSA arsenic determined by the speciation method to that measured by a routine CARB approved method showed good agreement. These results indicated the two methods were approximately equivalent for the monitoring of aerosol arsenic.

Size-fractionated aerosol samples were collected in the City of Industry and analyzed for their concentrations of As(III) and As(V). A greater portion

(about 75 percent) of both species was found in the fine particle fraction of the aerosol. The average As(III)/As(V) ratio observed in both the fine and coarse particle fractions was close to 1 (i.e., an equal mixture of the two species). For both particle size ranges, the As(III)/As(V) ratio varied from about 0.5 to about 2.9.

The presence of both inorganic arsenic species (i.e., arsenite and arsenate) in atmospheric particles suggest it may be possible to use a measurement of the As(III)/As(V) ratio, in collected ambient aerosols, as an indicator of the effective reduction-oxidation conditions present in the atmospheric environment. In addition, the chemical and physical information obtained from speciation measurements of this type will certainly help to more thoroughly evaluate source and sink strengths and to gain a better understanding of the complex geochemical cycles of arsenic and other related species in the environment.

Acknowledgements

The authors would like to thank Pat Harrington of the California Air Resources Board for his valuable contribution in conducting the sampling phase of this project. The authors would also like to thank the U.S. Postal Service for allowing the aerosol sampling equipment to be sited on the roof of its building in the City of Industry. This work was fully supported by the State of California, Air Resources Board.

Table I. Recovery of standards added to unexposed filters: Method A versus Method B.[a]

| | Average Recovery (%) | |
|---|---|---|
| Species | Method A[b] | Method B[c] |
| As(III) | 95 ± 7 | 86 ± 12 |
| As(V) | 100 ± 8 | 122 ± 7 |

a. 0.05 ml of ethanol was added prior to the addition of the leaching solution to reduce the hydrophobic nature of the PTFE filter material.

b. 200-400 ng of As(III) and As(V) added; n=12

c. 100-600 ng of As(III) and As(V) added; n=4

Table II. Comparison of two methods for the collection and analysis of total arsenic (sum of As(III) and As(V) in total suspended aerosol (concentrations in ng $m^{-3}$).

| Date collected | Collected by HVDVI[a,c] | Collected by standard Hi - Vol[b] |
|---|---|---|
| 12 Jan 87 | 74.1 | 69.4 |
| 13 Jan 87 | 22.3 | 24.4 |
| 14 Jan 87 | 11.0 | 5.5 |
| 15 Jan 87 | 6.2 | 4.4 |
| 19 Jan 87 | 9.9 | 16.2 |
| 20 Jan 87 | 8.9 | 12.1 |
| 21 Jan 87 | 8.9 | 11.8 |
| 22 Jan 87 | 24.8 | 34.0 |
| 25 Jan 87 | < 1.1 | 2.8 |
| 26 Jan 87 | 22.6 | 35.9 |
| 27 Jan 87 | 4.2 | 15.0 |
| 28 Jan 87 | 22.2 | 21.2 |
| 29 Jan 87 | 3.8 | 6.8 |
| 1 Feb 87 | 9.4 | 12.7 |
| 2 Feb 87 | 9.3 | 14.4 |
| 3 Feb 87 | 11.8 | 15.8 |

a. Employed Zefluor (PTFE) filters and was analyzed by method A.

b. Employed Whatman glass fiber filters and was analyzed by the CARB-HSL method no. 107, see reference 18.

c. Sum of both arsenic species in the fine and coarse particle fractions.

Table III. Arsenic(III) and As(V) concentrations (ng $m^{-3}$) and the As(III)/As(V) ratio observed in fine and coarse particles collected at the City of Industry in Los Angeles.[a]

| Date collected | As(III) ng $m^{-3}$ | | As(V) ng $m^{-3}$ | | As(III)/As(V) | |
|---|---|---|---|---|---|---|
| | Fine | Coarse | Fine | Coarse | Fine | Coarse |
| 12 Jan 87 | 44.0 | 4.8 | 18.7 | 6.6 | 2.4 | 0.7 |
| 13 Jan 87 | 10.9 | 1.8 | 6.6 | 3.0 | 1.7 | 0.6 |
| 14 Jan 87 | 4.2 | <1.8 | 4.6 | 2.2 | 0.9 | -- |
| 15 Jan 87 | 2.0 | <1.1 | 1.9 | 1.4 | 1.1 | -- |
| 19 Jan 87 | 2.9 | 1.4 | 3.4 | 2.2 | 0.9 | 0.6 |
| 20 Jan 87 | 5.3 | 1.2 | 2.4 | <1.0 | 2.2 | -- |
| 21 Jan 87 | 4.5 | 1.5 | 2.9 | <1.2 | 1.6 | -- |
| 22 Jan 87 | 14.1 | 4.1 | 4.9 | 1.7 | 2.9 | 2.4 |
| 25 Jan 87 | <1.2 | <0.9 | <1.0 | <1.0 | -- | -- |
| 26 Jan 87 | 10.2 | 2.2 | 5.9 | 4.3 | 1.7 | 0.5 |
| 27 Jan 87 | 1.5 | <1.0 | 1.8 | 0.9 | 0.8 | -- |
| 28 Jan 87 | 6.3 | <2.4 | 12.0 | 3.9 | 0.5 | -- |
| 29 Jan 87 | 2.2 | <0.9 | <0.9 | 1.6 | -- | -- |
| 1 Feb 87 | 3.7 | 1.0 | 3.4 | 1.3 | 1.1 | 0.8 |
| 2 Feb 87 | <1.7 | <1.7 | 7.0 | 2.3 | -- | -- |
| 3 Feb 87 | 4.2 | <1.1 | 6.1 | 1.5 | 0.7 | -- |
| $\bar{x}$ | 7.4 | 1.8 | 5.2 | 2.2 | 1.4 | 0.9 |
| $\pm$ $\sigma$b | $\pm$ 10.4 | $\pm$ 1.1 | $\pm$ 4.6 | $\pm$ 1.5 | $\pm$ 0.7 | $\pm$ 0.7 |

a. Values not corrected for 10 percent flow through coarse particle filter, see reference 15.

b. Includes less than values as equal to the detection limit indicated.

References

1. Department of Health Services, Health and Safety Code Sections 39650 et seq. (January 1984). California State Law Library, 914 Capitol Mall, Room 305, Sacramento, CA 95814.

2. D. J. Lisk, N. Y. State J. Med., 71 2541 (1971).

3. "Medical and Biological Effects of Environmental Pollutants: Arsenic", National Academy of Science, Washington. D.C. (1971) Chapter 5, p. 117.

4. "Medical and Biological Effects of Environmental Pollutants: Arsenic", National Academy of Science, Washington, D.C. (1971) p. 195.

5. S. Hernberg, "Origins of Human Cancer", Vol. 4, H. H. Hiatt, Ed; Cold Spring Harbour Laboratories, New York, NY. (1972) p. 147

6. W. Maenhaut, W. H. Zoller, R. A. Duce, G. L. Hoffman, J. Geophys. Res., 84 2421 (1979).

7. P. R. Walsh, R. A. Duce, J. L. Fasching, Environ. Sci. Technol., 11 163 (1977).

8. E. Sawicki, Arch. Environ. Hlth., 14 46 (1967).

9. G. R. Cass, and G. J. McRae, "Source-Receptor Reconciliation of South Coast Air Basin Particulate Air Quality Data," California Air Resources Board, Final Report, NTIS No. PB-82-250093.

10. Lowenbach and Schlesinger Associates, Inc., "Arsenic: A Preliminary Materials Balance," U.S. EPA Report 560/6-79-005 (1979).

11. D. J. Eatough, N. L. Eatough, M. W. Hill, N. F. Mankelson, J. Ryder, L. D. Hansen, R. G. Meisenheimer, J. W. Fischer, Atmos. Environ., 13 489 (1979).

12. P. A. Solomon, "Collection and Analysis Techniques for Studies of Armospheric Arsenic Species", Ph.D. Thesis, Dept. of Chemistry, University of Arizona, Tucson, Arizona (1984).

13. F. Perea, A. Karin Ahmed, "Respirable Particles: Impact of Airborne Fine Particles on Health and Environment" Ballinger Press, Cambridge, MA (1979).

14. J. H. Brown, K. M. Cook, F. G. Ney, T. Hatch, Amer. Jour. of Public Health, 40 450 (1950).

15. P. A. Solomon, J. L. Moyers, R. A. Fletcher, Aerosol Sci. Technol., 2 455 (1983).

16. "National Primary and Secondary Ambient Air Quality Standards," U. S. Environmental Protection Agency, Federal Register 36:8186 (1971).

17. M. R. Derrick, J. L. Moyers, Anal. Lett., 14 1637 (1981).

18. "Method 107," State of California, Air Resources Board, Haagen-Smit Laboratory, El Monte, California, 91731 (1986).

19. B. R. Appel, E. L. Kothny, Y. Tokiwa, M. Haik, J. J. Wesolowski, Fourth Quarterly Report to CARB (Contract No. ARB-5-1032), State of California, Air Resources Board, Sacramento, California (1977).

20. B. R. Appel, S. M. Wall, Y. Tokiwa and M. Haik, Atmos. Environ., 13 319 (1979).

21. R. W. Coutant, Environ. Sci. Technol., 11 (9) 873 (1977).

22. W. R. Pierson, W. W. Brachaczek, Atmos. Environ., Accepted for publication (July, 1987).